# ROLE OF QUATERNARY AMMONIUM COMPOUNDS AND ATMP ON BIOCIDAL EFFECT AND CORROSION INHIBITION OF MILD STEEL AND COPPER

S. Mohanan [#], S. Maruthamuthu, N. Kalaiselvi, R. Palaniappan*,
G. Venkatachari, N. Palaniswamy and M. Raghavan

*Central Electrochemical Research Institute*
*Council of Scientific and Industrial Research*
*Karaikudi-630 006, India*
**SPK College, Microbiology Department, Alwarkurichi, India.*
*[#] Corresponding author Fax:+91-4565-427779, 427713*
*E-mail address: Mohacecri@yahoo.com.in*

## ABSTRACT

Polyphosphates and organophosphonates are used as corrosion inhibitors in cooling waters. Biocides are also added to avoid microfouling by cooling water in industries. This work has been undertaken to find the influence of biocides such as quaternary ammonium compounds like cetyltrimethyl ammonium bromide (CTAB) and cetyl pyridinium bromide (CPB) on the corrosion of mild steel and copper in the presence of phosphonates. Cationic biocides are found to be highly efficient and the killing efficiency is found to be more for CTAB than CPB. On the other hand, CPB is found to be better than CTAB when biocides are used with inhibitor. Between the two metals chosen, the inhibition efficiency towards copper was observed to be more than mild steel due to the addition of CTAB and CPB with inhibitor. Polarization studies revealed that the presence of biocide CTAB with inhibitor gives the inhibition efficiency of about 80% for mild steel. CPB with inhibitor shows higher interference between biocide and inhibitor, whereas CPB alone is found to act as an inhibitor for copper (73%), which shows that the inhibitor might interfere in the biocidal action on copper.

**Keywords:** Biocides, inhibitor, mixed inhibitor, corrosion, interference

## INTRODUCTION

Biofouling and corrosion are the two important operational problems in heat exchangers and the associated cooling water system. Pipelines are known to be susceptible, especially to fouling-induced corrosion, due to their basic design characteristics and recirculation of water. Though biocides and inhibitors are used, problems have been noticed in various cooling water systems. The problems included flow blockage of pipes, punctures and unacceptable general corrosion rates of the system components.

Phosphates and chromates have normally been used as scale- and corrosion inhibitors in cooling water systems. In the latge 1970s and 1980s polyphosphates, phosphonates, carboxylic acids and polymeric phosphonates with zinc ions were used as corrosion inhibitors and antiscalants /1-5/. Polyphosphates have easily hydrolyzable P-O bonds resulting in the formation of orthophosphates. These orthophosphates are not good corrosion inhibitors but good feed for bacteria and algae, resulting in biofouling effects. Since phosphates act as good nutrients /6-8/ for bacteria and inhibitors such as chromate are toxic to the environment, the development of suitable chemicals that are capable of replacing phosphates and chromates has become highly essential. Phosphonates as such are not good corrosion inhibitors but in the presence of zinc ions they function as good corrosion inhibitors. Many industries are using different kinds of biocides to control microfouling in cooling water systems. Maintenance engineers are identifying suitable biocides for specific microorganisms like algae, SRB, and iron bacteria, etc., to prevent the microbial corrosion. For controlling fouling and corrosion, inhibitors are added continuously and biocides are added once a week or once in fifteen days. Hence, it is quite essential to find the interference between biocides and inhibitors in cooling water systems.

Organophosphonates are being used as inhibitors in cooling water for over a decade and the corrosion inhibition is decided by their ability to form a protective film on steel. The addition of tartrate with organophosphonic acid (2-carboxy ethyl phosphonic acid) and zinc metal cations /9/, the presence of fatty acids, triazoles /10/, combination of carboxy methyl phosphonic acid with carboxy ethyl phosphonic acid /11/, multivalent cations with molybdate /12/ have been reported for controlling corrosion of mild steel in aqueous environments. Generally, the efficiency of inhibitors for corrosion control and the efficiency of biocides on biological growth are being evaluated by chemists and microbiologists separately. However, there are fewer studies that are concerned with the interference between biocides and inhibitor for cooling water systems, and this subject needs extensive research and development. Though several studies on the use of phosphonates, viz. aminotrimethylene phosphonate (ATMP) with zinc ion as corrosion inhibitor have been reported in literature /9/, there is no report on the influence of inhibitor (ATMP) with some biocides except that of Maruthamuthu *et.al.* /13/.

In the present study, (ATMP) aminotrimethylene phosphonate as inhibitor and cetyl trimethyl ammonium bromide (CTAB) and cetylpyridinium bromide (CPB) as biocides have been selected to investigate the interaction between biocides and inhibitor. The possible interactions and the consequences of interaction between the chosen biocides and inhibitors are discussed in detail.

## MATERIALS AND METHODS

### Materials

#### *Composition of Materials*

Mild steel and copper, of the following composition, were chosen for corrosion evaluation.

The composition of mild steel is carbon 0.2%; phosphorus 0.4 – 0.5%; sulphur 0.02% - 0.03% and the rest of the iron and copper is 99% (commercial grade). Aminotrimethylene phosphonate (ATMP) 20 ppm with zinc 5 ppm was used as inhibitor. Cetyl trimethyl ammonium bromide (CTAB) and cetyl pyridinium bromide (CPB) were used as biocides. The stock solution of aminotrimethylene phosphonate (ATMP), zinc chloride, CTAB and CPB were prepared by dissolving 1 gm in 100 ml of sterile distilled water, which gave 10,000 ppm.

The mild steel and copper coupons with dimensions of 1.0 x 4.0 x 0.2 cm were mirror polished and used in the weight loss experiment and 1 sq.cm specimens were used for electrochemical studies. Pond water was used as the bacterial source. In all the experiments, the bacterial count was maintained in the range of log 5.01 bacteria/ml as initial count.

## Biocide/Inhibitor Evaluation

The 1% nutrient broth culture (24 hrs) was used for evaluation of biocides. Subsequently the biocides/inhibitors were added in various concentrations. Sampling was made at every 24 hr interval to enumerate viable bacterial counts employing pour plate techniques. Weighed mild steel and copper coupons were immersed in low chloride (200 ppm) electrolyte for a period of seven days. After seven days, the specimens were washed in distilled water and dried. After pickling, the changes in weight were calculated using the following formula:

$$\text{The percentage of inhibitor efficiency} = \frac{W_1 - W_2}{W_1} \times 100$$

where $W_1$ and $W_2$ are weight losses of steel in uninhibited and inhibited solutions respectively.

The corrosion rate of mild steel and copper was calculated by the following formula.

$$\text{Corrosion rate (mpy)} = \frac{534 \times \text{weight loss (mg)}}{\begin{matrix}\text{Density} \times & \text{Area} \times & \text{Time} \\ \text{(gm / cc)} & (\text{cm}^2) & \text{(hrs)}\end{matrix}}$$

## Electrochemical Measurements

A three-electrode cell assembly was used: 1 sq. cm mild steel and copper as the working electrode, a platinum foil of $3\text{cm}^2$ was used as the counter electrode and saturated calomel electrode (SCE) was used as the reference electrode. The polarisation studies were carried out using an EG & G PAR Model 173/potentiostat in combination with a Model 175 universal programmer and X-Y recorder. SCE was connected with test solution through a salt bridge. Potential (E) vs log current (i) plots were recorded at a sweep rate of 1 mV/sec. Tafel slopes ba and bc were determined from these plots.

## Systems Studied

### *System I (Biocides)*

To find the influence of biocides on corrosion process, cetyl trimethyl ammonium bromide (CTAB) and cetyl pyridinium bromide (CPB) were added in the bacteria-inoculated 1% broth and weight loss for mild steel and copper were determined after 7 days. In addition, bactericidal efficiency in the presence of biocides was also ascertained.

### *System II (Inhibitor)*

To find the inhibitor efficiency, amino trimethylene phosphonate (ATMP) with zinc chloride solutions (5ppm) was added in the bacteria-inoculated 1% broth and weight loss of mild steel and copper were determined after seven days. The bacterial killing efficiency of inhibitor was also studied.

### *System III (Biocides+Inhibitor)*

To find the interference between biocides (CTAB and CPB) and inhibitor (ATMP with zinc), both the biocide and inhibitor were added to 1% broth simultaneously. The inhibition efficiency was determined for mild steel and copper by weight loss technique. Subsequently, the influence of inhibitor on bacterial efficiency was also determined.

### *System IV (Inhibitor Addition after Killing Bacteria by Biocides)*

To avoid the interference between biocide and inhibitor, biocides were added in the bacteria-inoculated 1% broth to kill the bacteria. After 24 hrs, the inhibitor (ATMP + Zn) was added to the same 1% broth and corrosion rates were found out for mild steel and copper.

# RESULTS

## Bacterial killing efficiency

The bacterial killing efficiency of biocides and inhibitor is presented in Figures 1-5.

(1) CTAB: In the presence of 25 ppm CTAB, the complete (100%) killing time was about 24 hrs. 100% of bacteria were eliminated within 16 hrs. at 50 ppm concentration (Figures 1 and 2).

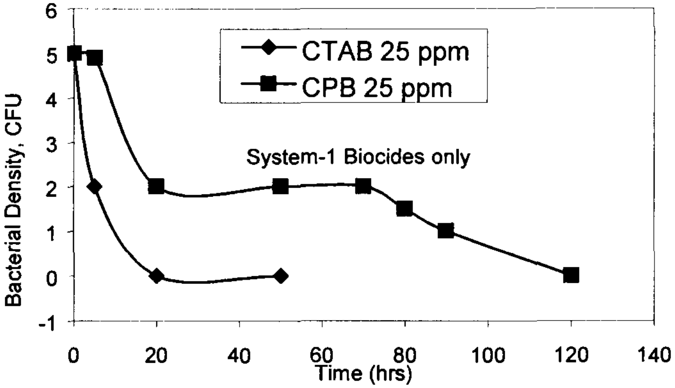


**Fig. 1:** The Bacterial Killing Time of Biocides

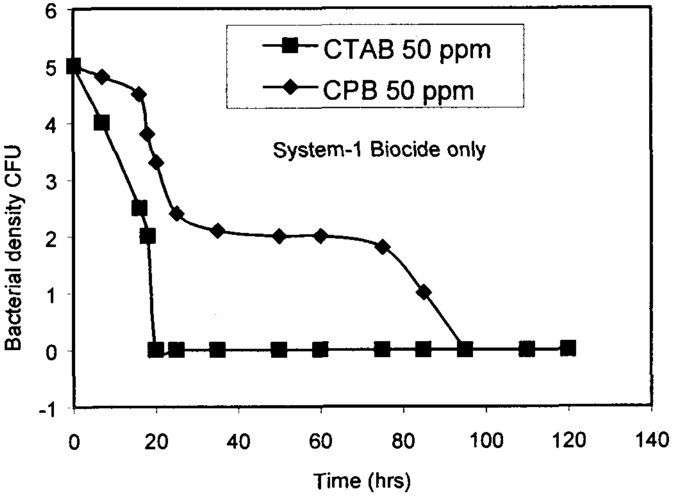


**Fig. 2:** The Bacterial Killing Time of Biocides

(2) CPB: Figs 1 and 2 show that the bactericidal activity of CPB was slow when compared to CTAB. In both 25 ppm and 50 ppm, the complete killing of bacteria was observed in 120 hrs and 96 hrs respectively.

(3) ATMP + Zn: Fig. 3 shows the bacterial killing efficiency of ATMP + Zn. The bacterial density was slightly reduced at 96 hrs, when compared to the initial counts. In a later period (after 96 hrs), inhibitor enhanced the

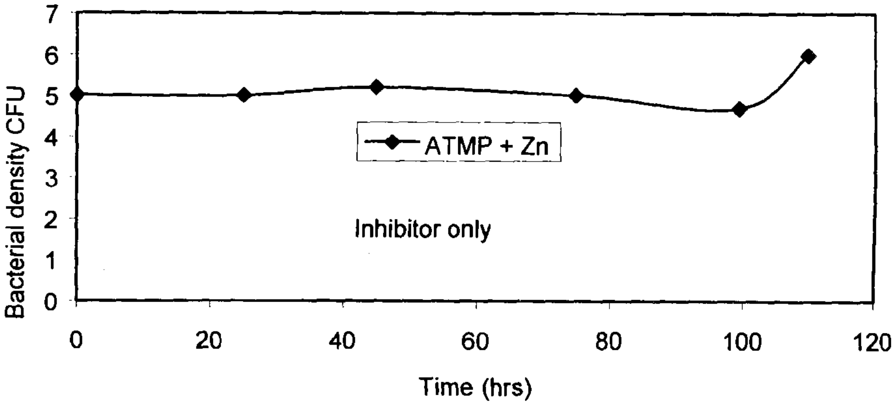


**Fig. 3:** Bactericidal Efficiency of Inhibitor

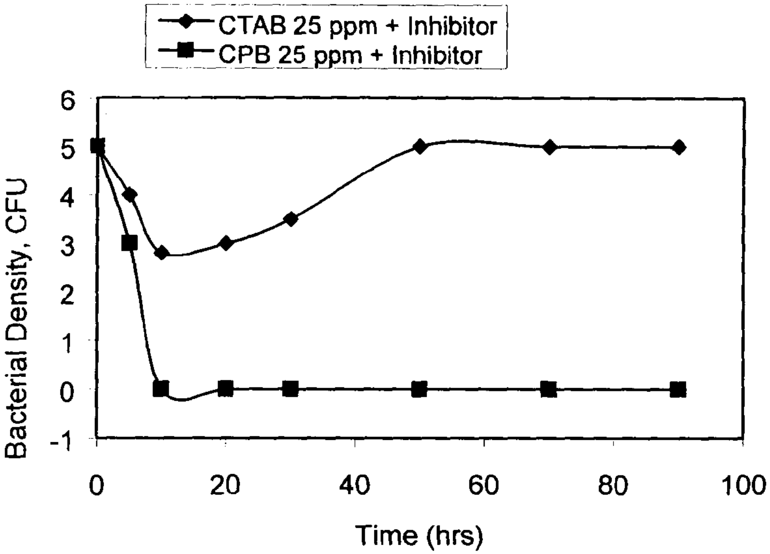


**Fig. 4:** The Bacterial Killing Time of Biocides with Inhibitor

growth of bacteria with time, which indicated that the inhibitor might act as a good nutrient for bacteria.

(4) CTAB + ATMP + Zn: While adding 25 ppm of biocide with inhibitor, the bacterial count was reduced from 5.01 log CFU / ml to 2.75 log CFU/ml within 6 hrs. Subsequently, bacterial density was increased to the initial level.

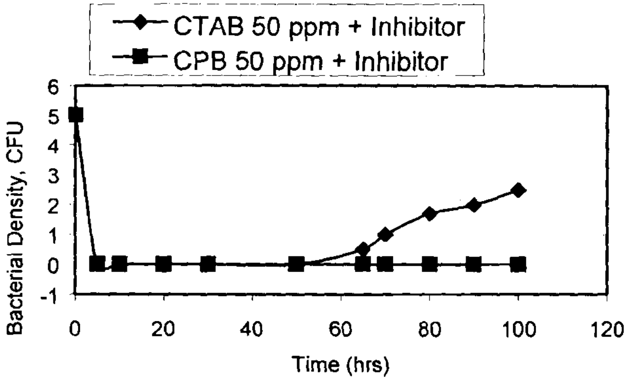


**Fig. 5:** The Bacterial Killing Time of Biocides with Inhibitor

In the presence of 50 ppm of biocide, there was a reduction in the bacterial counts to about nil after 48 hrs. of observation. Besides, it enhanced the growth of bacteria slowly about 2.2 log CFU/ml at 110 hrs.

(5) CPB + ATMP + Zn: Regarding the killing efficiency of cetylpyridine bromide (CPB) with inhibitors in the concentration of 25 ppm and 50 ppm, all bacteria were killed within 10 hrs. The results revealed that CTAB acted as a good biocide when compared to CPB as an individual component. But CPB acted as a good biocidal system when compared to CTAB when mixed with inhibitor.

## Corrosion inhibition

### *Mild Steel*

*1. Effect of biocides on corrosion*

The corrosion rates of mild steel in the presence of biocides are presented in Fig. 6. CTAB decreased the corrosion rate and showed an inhibition efficiency of 33% in the presence of 50 ppm and 4% in presence of 25 ppm. In the presence of CPB the efficiency was about 3% and 14% in 25 ppm and 50 ppm respectively.

*2. Effect of Inhibitor on Corrosion*

Fig.7 shows that ATMP + Zn acts as a good corrosion inhibitor and the efficiency was about 96%.

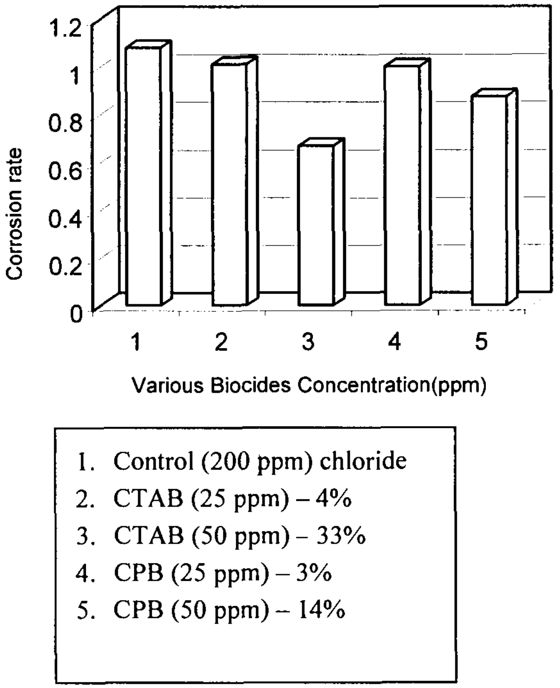


**Fig. 6:** Corrosion Rate of Mild Steel in the Presence of Biocides (% = corrosion inhibition); Mild Steel System I

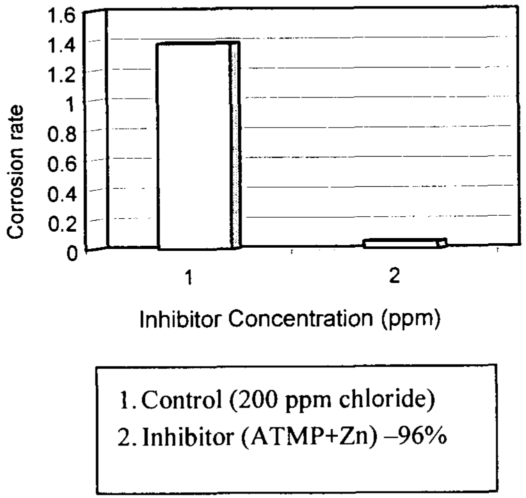
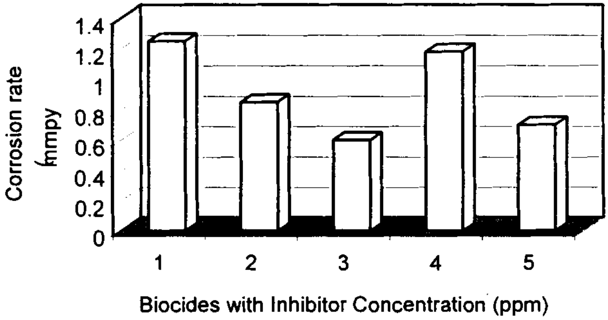


**Fig. 7:** Inhibitor Efficiency on Mild Steel in the Presence of Aminotrimethylene Phosphonate + Zinc (Atmp + Zn): Mild Steel System II.

*3. Effect of biocides with inhibitor*

In the presence of inhibitor with biocides (Fig. 8) the corrosion inhibition efficiency was about 58% in the presence of 50 ppm and 38% in the presence of 25 ppm of CTAB. Inhibitor with CPB inhibited the mild steel corrosion and provided about 45% inhibition efficiency in the presence of 50 ppm and 4% efficiency in the presence of 25 ppm of biocide (CPB).

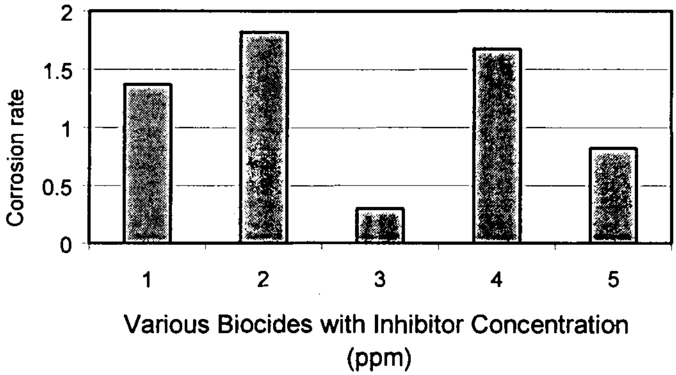


1) Control (200 ppm chloride)
2) CTAB (25 ppm)+ATMP +Zn –38%
3) CTAB (50ppm)+ATMP+Zn –58%
4) CPB (25ppm)+ATMP+Zn – 31%
5) CPB (50ppm)+ATMP+Zn –45%

**Fig. 8:** Effect of Biocides + Inhibitor on Mild Steel Corrosion Mild Steel System III: Biocides + Inhibitors.

*4. Effect of inhibitor addition after killing bacteria by biocides*

In the CTAB system, the corrosion inhibition efficiency was about –35%, and in the presence of CPB the efficiency was about –24%. With the addition of inhibitor to the CTAB system, the corrosion inhibition efficiency was about 75.3%, whereas CPB with inhibitor showed an efficiency of about 38% for mild steel (Fig. 9).



1. Control (200 ppm chloride)
2. CTAB (25ppm)+ATMP+Zn -35%
3. CTAB (50ppm)+ATMP+Zn -75%
4. CPB (25ppm)+ATMP+Zn -24%
5. CPB (50ppm)+ATMP+Zn -38%

**Fig. 9:** Effect of Inhibitor Addition after Killing Bacteria by Biocides Mild Steel System IV

### *Copper*

*1. Effect of biocide on corrosion*

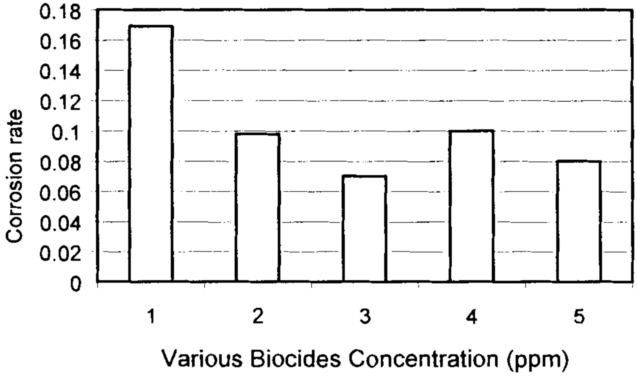
Fig. 10 shows inhibition efficiency of CTAB, which was about 59% in 50 ppm and 42% in 25 ppm. While using CPB, the inhibition efficiency was about 53% and 41% in the presence of 50 ppm and 25 ppm respectively.

*2. Effect of inhibitor on corrosion*

Fig. 11 shows the inhibition efficiency of ATMP + zinc for copper. The inhibition efficiency was about 13%.

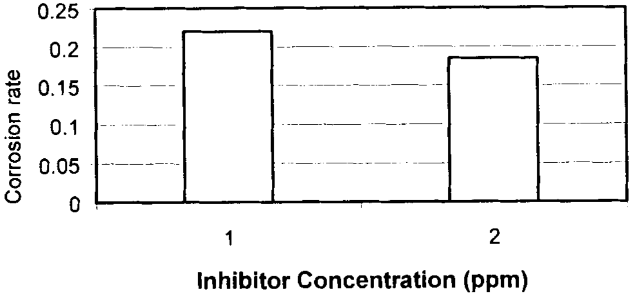
*3. Effect of biocides with inhibitor*

Fig. 12 shows the inhibition efficiency of biocides with inhibitor for copper. In the presence of both inhibitor and biocide system, the inhibition efficiency was about 94% at 50 ppm and 89% at 25 ppm of CTAB. CPB with inhibitor showed inhibition efficiency of about 88% and 82% in the presence of 50 ppm and 25 ppm of CPB, respectively.



1. Control (200 ppm chloride)
2. CTAB (25ppm) – 42%
3. CTAB (50ppm) – 59%
4. CPB (25ppm) – 41%
5. CPB (50ppm) – 53%

**Fig. 10:** Effect of Biocides on Corrosion of Copper
Copper System – I: Biocides Only



1. Control (200ppm chloride)
2. ATMP+Zn – 13%

**Fig. 11:** Effect of Inhibitor (ATMP + Zn) on Copper Corrosion.
Copper System II: Inhibitor Only

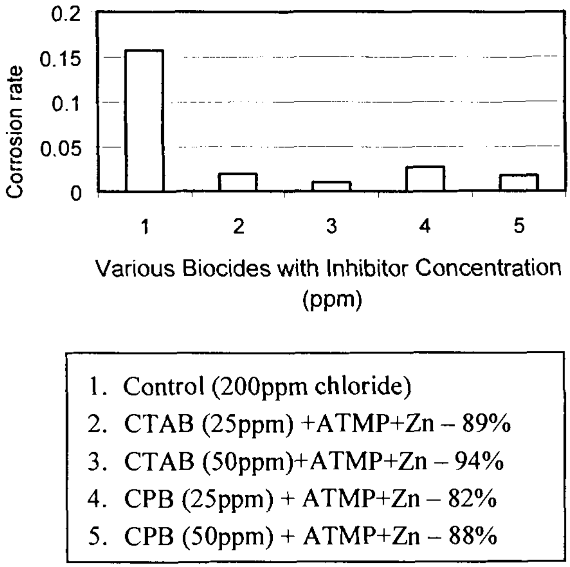


**Fig. 12:** Inhibition Efficiency of Biocides and Inhibitor on Copper Copper System III: Biocide + Inhibitor

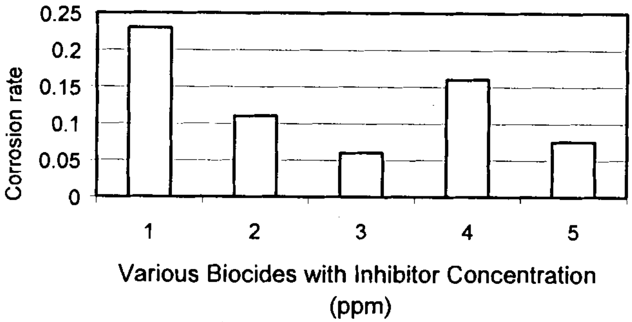
*4. Effect of inhibitor addition after killing bacteria by biocides*

Corrosion inhibition efficiency of CTAB was about 48% and CPB was about 30%. The mixing of inhibitor in the biocide CTAB treated water gave 78% of corrosion inhibition. In the presence of CPB treated water with inhibitor, the inhibitor efficiency was about 70% (Fig. 13).

## Polarisation studies:

### *Mild Steel*

In biocide-treated water, the corrosion currents were observed to be around 10 $\mu A/cm^2$, while on addition of inhibitor to the biocide-treated system, the corrosion current was found to be lower in the presence of inhibitor. With CPB-treated water, the corrosion current was about 4.7 $\mu A/cm^2$ whereas, using inhibitor with CTAB-treated water, the corrosion current was about 1.95 $\mu A/cm^2$. The corrosion potential for control was –757 mV vs SCE in the presence of biocide-treated water; the corrosion potential shifted to the positive side in the range between 50 and 70 mV. In the presence of inhibitor with CPB the corrosion potential was –727 mV. However, in the presence of CTAB with inhibitor, the corrosion potential was –646 mV.



1. Control (200ppm Chloride)
2. CTAB (25ppm) +ATMP+Zn – 48%
3. CTAB (50ppm) + ATMP+Zn – 78%
4. CPB (25ppm) + ATMP + Zn – 30%
5. CPB (50ppm) + ATMP + Zn – 70%

**Fig. 13:** Effect of Inhibitor Addition After Killing Bacteria by Biocides Copper System IV

## Copper

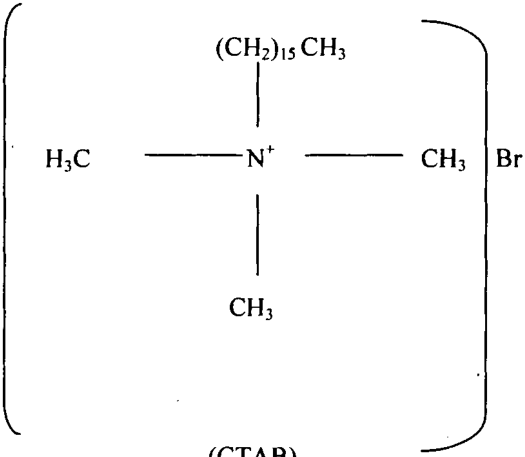
The corrosion current from the polarization study was about 0.95 μA/cm$^2$ in control. In biocide CPB-treated water, the corrosion current was about 0.25 μA/cm$^2$. With the addition of inhibitor to CPB-treated water systems, the corrosion current was 0.666 μA/cm$^2$ and where inhibitor was added to CTAB-treated water systems, the corrosion current was about 0.098 μA/cm$^2$. The corrosion potential for control was –72 mV. In the presence of biocide (CPB)-treated water, the corrosion potential was shifted to the positive side (–33 mV). The corrosion potential in CTAB-treated systems was found to be –103 mV. In the presence of inhibitor with CPB-treated systems, the corrosion potential observed was –93 mV. However, using inhibitor with CTAB treated system, the corrosion potential was –15 mV.

## DISCUSSION

Several studies on the use of phosphonic acid, viz. aminotrimethylene phosphonic acid (ATMP), hydroxy ethyl diphosphonic acid (HEDP), hydroxy phosphono acetic acid (HPA), etc., as corrosion inhibitors have been reported /1, 3, 14/. Several investigations have also been carried out on the use of biocides to control various pelagic microbes or sessile microbes in cooling water systems /15-17/. However, no study has been reported so far on the interference between inhibitor and biocides.

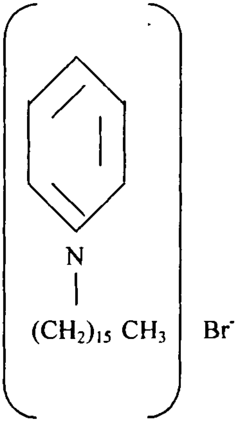
## Bacterial Killing Efficiency

The bacterial killing efficiency of biocides (CTAB, CPB) with and without inhibitor was investigated (Figs. 1-5). Inhibitor increased the bacterial density from 5.01 log CFU/ml with time. It is well known that both the biocides tested in the present study are cationic in nature, which disturbs the arrangement of phospholipid molecules of bacteria and turns the bacteria into lysis condition. The present study shows that the killing efficiency of CTAB is better than CPB, which may be understood as follows: With the addition of inhibitor (ATMP + Zn), the biocide CTAB enhanced the growth of bacteria, i.e. the biocide CTAB with inhibitor lost its bactericidal activity against bacteria. But CPB acted as a good biocide when combined with ATMP, i.e. CPB has acquired some improved characteristics, when combined with inhibitor, in terms of higher killing efficiency. Evidently system-3 indicated that phosphonate could be utilized by bacteria /6,18/. In the present study, it is understood that the biocide CTAB lost its activity against bacteria, when it was combined with the inhibitor. Besides catalyzing the growth of bacteria, CTAB, when the killing efficiency was analyzed, formed a greenish yellow colour in some colonies of bacteria within a period of 6 hrs. This may be attributed to the accumulation of bromine inside the cells of the bacteria. This may be explained as a function of tolerance or resistance of some bacterial colonies against CTAB /19/.



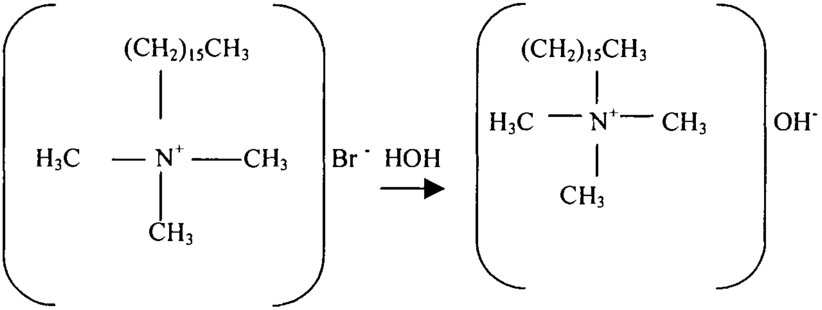
$$\left[ H_3C - \overset{\overset{\displaystyle (CH_2)_{15}CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^+}} - CH_3 \right] Br$$

(CTAB)



(CPB)

CTAB, an aliphatic quaternary ammonium salt, is highly ionic in nature, due to which the $Br^{(-)}$ found out of the coordination sphere is readily available for removal/reaction with suitable reagents. In spite of being a mild base (compared to that of CPB), it undergoes hydrolysis or substitution reaction, due to the very high dielectric constant of polar water molecule.



The removal of $Br^-$ in water may ultimately result in the formation of HBr or may even lead to the formation of bromine molecule in the form of gas.

Therefore, it is possible that the easily available form of bromine (either as HBr or as $Br_2 \uparrow$ ) enters inside the cell wall of the bacteria, leading to better killing efficiency. CPB, an aromatic quaternary ammonium salt, due to the presence of conjugation in terms of aromatic nature, will always try to exhibit maximum stability. The presence of delocalised electrons stabilizes the compound and for that stabilization process, the presence of Br- is necessarily required. Therefore, the compound will exist as such, to maintain the stability.

In the case of a combination of biocide and inhibitor, the reverse trend was observed, i.e. CPB was found to have more killing efficiency than CTAB. The reason is unknown, so further work is needed.

## Corrosion Inhibition Efficiency

### *Mild Steel*

A combination of ATMP with zinc ion acts as a good inhibitor. Biocides reduced the inhibition efficiency upon combination with inhibitor. However, biocides when added separately were found to reduce the corrosion rate slightly. Therefore, corrosion inhibition with ATMP + zinc ion may be attributed to the formation of passive film with zinc hydroxide on mild steel surface.

### *Copper*

The corrosion inhibition was estimated to be about 13% in the presence of ATMP + zinc. On the other hand, when biocides were used along with inhibitors, the copper corrosion was found to be about 50% in various concentrations. It was also noticed that the biocides enhanced the inhibition efficiency of copper when combined with the inhibitor. CTAB in 50 ppm enhanced the inhibition of copper to 94% when compared to CPB (88%). Hence, it is an indication that the acceleration of copper corrosion by phosphate was suppressed by cationic biocides.

For the iron phosphonate system, phosphonate forms a passive film while for copper it forms a complex with copper and hence, inhibition is not observed.

On the contrary, copper, which does not have a proper passivation film, will readily form cuproammonium salts /20/ and copper pyridine complex /21/. The existence of even pentacoordinate copper (II) complexes has already been established with pyridine /21/ and therefore Cu is now tightly surrounded by ligands, and hence is protected from Br- attack. The preference of Cu to form complexes with NH4 and pyridinium ions will be higher than forming copper halides due to known reasons.

Therefore, the inhibition efficiency of Cu will be greater due to the addition of CTAB and CPB. The following is the corrosion inhibition order along with the presence of biocide and inhibitor in low chloride media.

Fe > Cu (with inhibitor)
Cu > Fe (with inhibitor and biocides)

In system 4, the biocide-treated water system enhanced the corrosion rate of mild steel when compared to the direct influence of biocide on mild steel (system 1). In copper, the corrosion rate did not vary much between system-1 and system-4.

The addition of inhibitor to biocide (CTAB) treated water (system-4) resulted in the corrosion inhibition efficiency of about 75% for mild steel, which was higher when compared to biocide + inhibitor mixed system (system 2). But the CPB treated water system with inhibitor gave a corrosion inhibition efficiency of 38%, which was lower than system-2 (inhibitor +

biocide mixed system). Hence it can be concluded that while adding inhibitor in CTAB- and CPB-treated water systems, the corrosion inhibition efficiency was found to improve for mild steel and the efficiency was decreased for copper compared to system-2. Therefore, it may be considered that the disturbance of bromide ions on mild steel may be less in the presence of ATMP+Zn, and thus the corrosion inhibition efficiency may be improved. Similarly, the formation of copper pyridinium complex may be ascribed, in system-4, as a factor responsible for the lower inhibition efficiency on copper.

## CONCLUSIONS

Cationic biocides in general are found to be highly efficient in microbial killing; they act as a corrosion inhibitor when bacteria are present in pond water. Also, it is understood that the aliphatic (CTAB) and aromatic nature (CPB) of the biocides in terms of their reactivity and stability plays a vital role during their combination with inhibitors ATMP/Zn and metals (Fe, Cu). The better bacterial killing efficiency and inhibition efficiency of different conditions were dealt with in terms of appropriate reaction mechanisms, which are in excellent agreement with the theoretical predictions and the practical observations. Hence, the present investigation leads to the following conclusions regarding the biocidal and inhibition efficiencies of CTAB and CPB over mild steel and copper.

i) Microbial killing efficiency is greater for CTAB than for CPB.
ii) CPB acts better than CTAB, when biocides are taken with inhibitor with respect to both mild steel and copper.
iii) The ionization of biocides to produce bromide (either as KBr or as $Br_2$) is found to be responsible for the bacterial killing process.
iv) Mild steel exhibits more corrosion inhibition rather than copper in the presence of inhibitor.
v) Copper performs better than mild steel when biocides are combined with inhibitor.

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